STEADY-STATE AND DYNAMIC SIMULATION OF THE PROCESS OF EXTRACTIVE DISTILLATION OF 1,3-BUTADIEBE FROM THE C$_4$-CUT

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ABSTRACT

Separation of 1,3-butadiene from the C$_4$-cut is not possible by conventional distillation due to formation of several azeotropic mixtures and very close boiling points of the components. The BASF 1,3-butadiene extraction process takes advantage of highly improved relative volatilities of most of the components in the presence of a selective solvent. The solvent is n-methylpyrrolidone (NMP) which contains approximately 8.3% water. In the present work, the 1,3-butadiene extraction process is simulated in both steady-state and dynamic conditions. The results of the steady-state simulation are compared with plant data and show a good agreement between these values. It was found that the NRTL equation of state is able to predict the experimental data satisfactorily throughout the process. The binary interaction coefficients of the components were tuned in this study such that the equation of state best fits the real equilibrium data. The dynamic model is then used to study the effects of disturbances and changing effective parameters on the process.

1 INTRODUCTION

1,3-Butadiene is a colorless, non-corrosive gas with mild aromatic or gasoline-like odor with the boiling point of –4.4° C at atmospheric pressure and liquid density of 611 Kg/m^3 at 20°C. It is used primarily as a co-monomer for producing styrene-butadiene rubber. Separation of 1,3-butadiene from the C$_4$-cut by conventional distillation is not possible due to the formation of several azeotropes and very close boiling points of most of the components. The alternative process for separation of 1,3-butadiene from the C$_4$-cut is extractive distillation. Extractive distillation is defined as distillation in the presence of a miscible, high boiling, relatively nonvolatile compound (i.e., the solvent) which forms no azeotrope with other components in the mixture. This separation technique is widely used in chemical and petrochemical industries for separating azeotropic, close-boiling and low relative volatility components from the mixture. In extractive distillation, the solvent is chosen to interact differently with the compo-

nents of the original mixture, thereby, altering their relative volatilities. Since these interactions occur predominantly in the liquid phase, the solvent is continuously added close to the top of the extractive distillation column such that an appreciable amount of solvent is present in the liquid phase on all the trays below.

N-methylpyrrolidone (NMP), a solvent with high solubility and selectivity for unsaturated compounds which has been used successfully in numerous industrial plants, proved its merits for 1,3-butadiene extraction. The BASF process for the recovery of high purity 1,3-butadiene from C$_4$-cut employs NMP as the selective solvent. Selectivity can be defined as the ability of the solvent to pick up the desired component in the feed as compared to other components. Table 1 gives the selectivity of NMP in different mixtures.

Table 1: Selectivity of NMP (40° C, 760 mm Hg)

Mixture	Selectivity
1,3-Butadiene / i-Butane	8.52
1,3-Butadiene / n-Butane	4.37
1,3-Butadiene / 1-Butene	2.66
1,3-Butadiene / 2-cis-Butene	1.65
1,3-Butadiene / Propyne	1.09
1,2-Butadiene / 1,3-Butadiene	1.88
1-Butyne / 1,3-Butadiene	2.46
Vinyl acetylene / 1,3-Butadiene	5.44

The high selectivity of NMP for 1,3-butadiene versus the less soluble butanes and because of more readily soluble acetylene compounds versus butadiene in the solvent makes NMP an ideal solvent in the recovery of butadiene with optimum purity. The selectivity of NMP is also sufficient to separate 1,2-butadiene from 1,3-butadiene. Selectivity of NMP for propyne is relatively low. However, the difference between the boiling points is large enough to

separate propyne from 1,3-butadiene down to the permissible level.

In addition to the selectivity, other properties of NMP such as low vapor pressure, stability and proper solubility for acetylenes has made this solvent the best for extraction of 1,3-butadiene.

2 PROCESS DESCRIPTION

The block flow diagram of butadiene extraction process is shown in Figure 1. This process include two major process steps:

- The extractive distillation section
- The distillation section
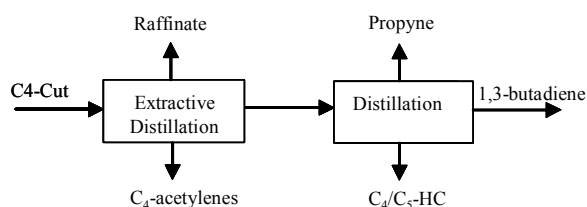
These sections are described below.

Figure 1: Block flow diagram of 1,3-butadiene extraction process

The extractive distillation section consists of the following subsections:

- First extractive distillation column
- Second extractive distillation column
- Degassing

Butanes and butenes, which have the smallest solubility in NMP, are separated as the overhead product (raffinate) of the extractive distillation section. A vapor stream consisting mainly of 1,3-butadiene and C_4-acetylenes is sent to the second extractive distillation step. In this tower the more soluble acetylenic components are removed by means of fresh NMP. Crude butadiene is withdrawn as the overhead product of the second extractive distillation step. The C_4-acetylenes are fully absorbed by NMP and are withdrawn from the degassing section. In the degassing section dissolved hydrocarbons are completely removed from the solvent.

The distillation section comprises the following subsections:

- Propyne distillation column
- Final distillation column

Crude butadiene obtained from the extractive distillation is further purified in two subsequent distillation towers. In the first distillation tower propyne together with some 1,3-butadiene for dilution is withdrawn as the overhead product. In the second distillation tower a mixture containing 1,2-butadiene and C_5-hydrocarbons are separated as the bottom product. The 1,3-butadiene product is withdrawn from the overhead of the final distillation tower.

2.1 Process Flow Diagram

The process flow diagram of BASF 1,3-butadiene extraction process which has been simulated in the present work is shown in Figure 2. According to this diagram, the liquid C_4-fraction from battery limit is fed to the feed surge drum where fluctuations of the flow to the process can be diminished. The feed is vaporized in the reboilers which are heated up with hot NMP, routed from the bottom of the degassing tower. The required flow rate of C_4-hydrocarbons to the main washer is measured in the vapor line connecting to drum with main washer and adjusted by a flow controller. Vaporized C_4-cut enters the main washer at the bottom together with the top gas from the rectifier and is counter-currently washed with NMP. 1,3-Butadiene is almost completely absorbed in this tower. The overhead product from the main washer contains the bulk of propane, propene, propadiene, butanes and butanes present in the C_4-cut feed stock of the plant.

The solvent (NMP) with approximately 8.3% (w/w) water, is fed to the top of the main washer. The solvent flow is also controlled by a flow controller. The solvent withdrawn from the bottom of the main washer is pumped to the top of the rectifier. The level controller on the main washer controls the flow of the solvent.

In the upper part of the rectifier, the less soluble (i.e., more volatile) butene is stripped from the solvent by a counter-current vapor stream of the more soluble butadiene rising from the bottom. The gaseous mixture of 1,3-butadiene and butene leaves the top of the rectifier and is fed back to the bottom of the main washer. The concentration of 1,3-butadiene in the vapor rises to its maximum between the rectifiers upper and lower part. From this location a butadiene-rich side-stream is withdrawn and fed into the bottom of the after-washer.

The bottoms of the rectifier is divided into two streams. The solvent loaded with hydrocarbons is drawn off from one compartment and routed to a heat exchanger where it is heated up on the tube side. Then, it is flashed into the second compartment of the rectifier bottom where by means of pre-degassing a considerable amount of the dissolved hydrocarbons is vaporized.

The remaining butadiene which still contains C_4-acetylenes is withdrawn as a gaseous side-stream from the rectifier and fed into the bottom of the after-washer. In this column, butenyne (vinylacetylene) and 1-butyne
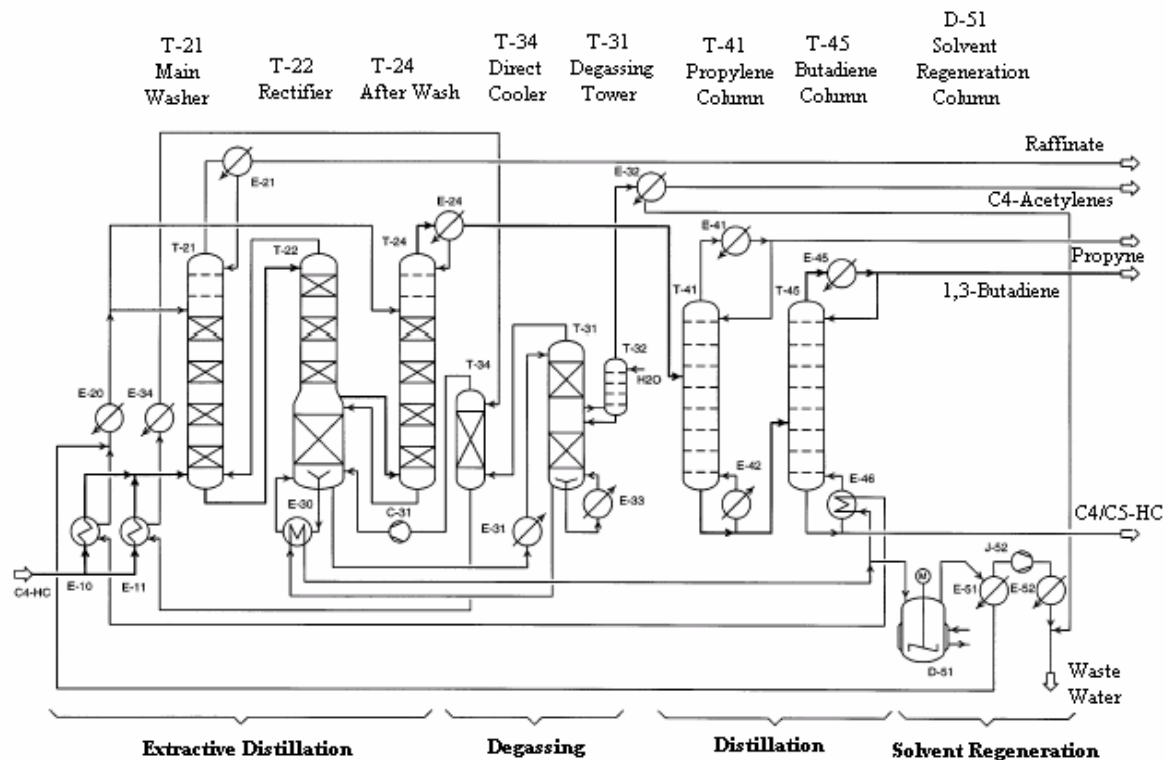
Figure 2: Simplified process flow diagram of 1,3-butadiene extraction process

(ethylacetylene) are removed from 1,3-butadiene. The C_4-acetylenes are more soluble in NMP (i.e., less volatile) than 1,3-butadiene and are removed counter-currently with fresh solvent that is fed to the top of the column. The C_4-acetylenes absorbed in the solvent are drawn from the bottom of the after-washer and transferred by the after-washer pump to the rectifier. Water which is presented in the overhead vapor of this tower is separated from the organic phase in the bootleg of an accumulator.

The pre-degassing solvent from the rectifier is heated up again in solvent heater and flashed into the degassing tower. The hydrocarbons dissolved in the loaded solvent from the rectifier have to be separated completely before the solvent is recycled to the extractive distillation section. Degassing of the solvent is carried out in the degassing tower by stripping with solvent and water evaporated in the reboiler. The crude butadiene is fed to the propyne distillation column and the bottom product of the propyne column is fed into the final distillation column where components with lower volatility than 1,3-butadiene are separated as the bottoms product while 1,3-butadiene is withdrawn as the overhead product.

3 MODELING

The first step in process simulation is to determine the suitable thermodynamic system, i.e., a proper equation of state with attention to the components and process conditions. For polar or non-ideal chemical systems usually binary thermodynamic systems are employed. In this way, an equation of state (such as ideal gas, Peng-Robinson, Soave-Redlich-Kwang, etc.) is used to predict the vapor fugacity coefficient while another equation of state (usually based on the activity model) is employed for the liquid phase. In the present study, NRTL is used as the main equation of state, for liquid phase with its binary interaction coefficients being modified in order to best represent the vapor-liquid equilibrium behavior of the system. In the two distillation towers Peng-Robinson equation of state is used as the thermodynamic model because of the absence of NMP. The vapor phase is assumed to be ideal throughout this work.

A mathematical model have been developed in the present study to represent the behavior of the multicompo-

nent columns. The trays in each column are numbered from bottom to the top. A general sketch of the nth tray of a multicomponent separation column, with considering side draws and feeds to each stage, is shown in Figure 3.
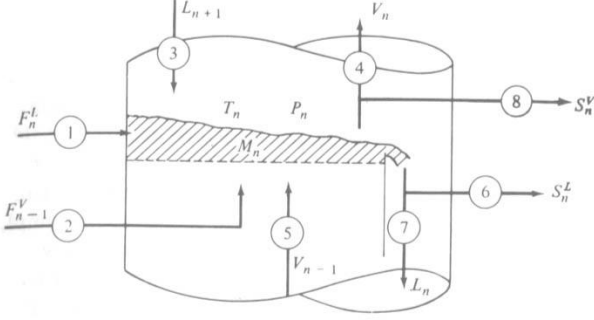

Figure 3: Schematic of nth tray of a multicomponent tower.

In the modeling approach adopted in this work, five types of equations are required for a complete description of each stage. These equations are: total continuity, component mass balance, vapor-liquid-equilibrium (VLE) relationship for each component, stoichiometric constraints and the energy balance. These equations are formulated as follows for each tray:

1) Total continuity at stage n:

$$\frac{dM_n}{dt} = L_{n+1} + F_n^L + F_{n-1}^V + V_{n-1} - V_n - L_n - S_n^L - S_n^V \quad (1)$$

2) Component mass balance:

$$\frac{d(M_n x_{i,n})}{dt} = L_{n+1}x_{i,n+1} + F_n^L x_{i,n}^F + F_{n-1}^V y_{i,n-1}^F + V_{n-1}y_{i,n-1}$$
$$-V_n y_{i,n} - L_n x_{i,n} - S_n^L x_{i,n} - S_n^V y_{i,n} \quad (2)$$

3) VLE relationship for each component:

$$K_i = \frac{y_{i,n}}{x_{i,n}} \quad (3)$$

4) Stoichiometric constraints:

$$\sum x_{i,n} = \sum y_{i,n} = 1 \quad (4)$$

5) Energy balance

$$\frac{d(M_n h_n)}{dt} = L_{n+1}h_{n+1} + F_n^L h_n^F + F_{n-1}^V H_{n-1}^F + V_{n-1}H_{n-1}$$
$$-V_n H_n - L_n h_n - S_n^L h_n - S_n^V H_n \quad (5)$$

The liquid and vapor streams leaving any given stage are assumed to be in thermodynamic phase equilibrium with each other.

4   RESULTS AND DISCUSSION

The model equations were solved for the butadiene extraction plant of Amir Kabir Petrochemical Company. The feed composition is shown in Table 2. The temperature and pressure of the feed are 30 °C and 700 KPa, respectively.

Table 2: Composition of the feed

Component	Mass fraction (%)
Propane	2.11×10^{-3}
Propene	1.00×10^{-2}
Methyl-Acetylene	6.13×10^{-2}
Propadiene	4.83×10^{-2}
n-Butane	7.61
i-Butane	3.54
1-Butene	6.32
i-Butene	23.40
Transe-2-Butene	3.27
cis-2-Butene	2.58
1,3-Butadiene	50.43
1,2-Butadiene	0.29
Ethyl-Acetylene	0.36
Vinyl-Acetylene	1.91
Water	0.00
NMP	0.00

4.1 Steady-State Simulation

It is obvious that in the steady-state simulation, the change in the liquid holdup of trays has to be vanished. As a result, the derivatives in the left hand sides of equations (1), (2) and (5) become zero in such a condition. The model then reduces to solution of a set of nonlinear algebraic equations. Therefore, temperature and compositions become independent of time and uniform at each stage in the steady-state mode.

The results of the steady state simulation for some main parameters of the process are shown in Tables 3 to 7. The corresponding operating values are also given in these tables. As could be seen from these tables, there is a good agreement between the results of the simulation and actual plant data. The model is therefore validated.

Table 3: Comparison between operating and simulated values in the main washer column

Parameter	Simulated value	Operating value
Mass fraction of 1,3-butadiene in overhead stream	0.18	0.19
Mass fraction of i-butene in overhead stream	53.14	49.96
Mass fraction of 1,3-butadiene in bottom stream	69.75	73.18
Mass fraction of i-butene in bottom stream	8.27	7.54
Temperature of bottom stream (°C)	42.4	43.3

Table 4: Comparison between operating and simulated values in the rectifier tower

Parameter	Simulated value	Operating value
Mass fraction of 1,3-butadiene in overhead stream	69.64	68.92
Mass fraction of 1-butene in overhead stream	3.4	3.6
Mass fraction of i-butene in overhead stream	16.7	17.28
Mass fraction of butane in overhead stream	1.8	1.93
Mass fraction of 1,3-butadiene in overhead stream	78.6	78.9

Table 5: Comparison between operating and simulated values in the after washer tower

Parameter	Simulated value	Operating value
Mass fraction of 1,3-butadiene in overhead stream	98.7	99.08
Mass fraction of 1-butyne in overhead stream	0.04	0.00
Mass fraction of butenyne in overhead stream	0.03	0.00
Mass fraction of 1,2-butadiene in overhead stream	0.41	0.43

Table 6: Comparison between operating and simulated values in the degassing tower

Parameter	Simulated value	Operating value
Mass fraction of 1,3-butadiene in overhead stream	81.15	80.79
Mass fraction of 1,2-butadiene in overhead stream	6.48	6.39
Temperature of overhead stream (°C)	99.14	99.4

Table 7: Comparison between operating and simulated values in final distillation tower

Parameter	Simulated value	Operating value
Mass fraction of 1,3-butadiene in outletstream	99.46	99.7
Mass fraction of i-butene in outlet stream	0.0	0.045
Mass fraction of transe-2-butene in outlet stream	0.022	0.21
Mass fraction of cis-2-butene in outlet stream	0.30	0.22

4.2 Dynamic Simulation

In the case of dynamic simulation, equation (1) to (5) have to be solved simultaneously in the form shown above. In the dynamic mode, the change in the liquid holdup on the trays should be considered. Since the derivatives are present in this mode, the set of ordinary differential equations have to be solved to find the dynamic response of the plant to the changes in operating conditions. In order to simplify the model, it has been assumed that the vapor holdup on each tray is negligible. In dynamic conditions, the equations of the controllers have to be considered and solved along the equations of the equipments. The controllers in this study are assumed to be proportional-integral-derivative (PID). The output of these controllers is given by:

$$C(t) = K_c \varepsilon(t) + \tau_D \frac{d\varepsilon}{dt} + \frac{1}{\tau_I} \int_0^t \varepsilon(t)dt + C_s \quad (6)$$

The coefficients of equation (6) (gains) should be tuned for each controller before the final run.

In order to study the process, a series of effective parameters are recognized and dynamic response of the process is studied when changing these parameters. These investigations are summarized below:

In separation of 1,3-butadiene from the C_4-cut, the flow rate of the solvent has a considerable effect on the process, especially in the main washer column. Figure 4 illustrates the change in the liquid level of the column when the flow rate of solvent to the main washer is increased by 15% increasing. It is seen in this figure that the liquid level of the column increases due to the increase in the liquid volume flow rate to the column. The comparison between the period of increase shown in Figure 4 and the corresponding time observed in the real process reveals a good agreement between the results of simulation and the plant data.
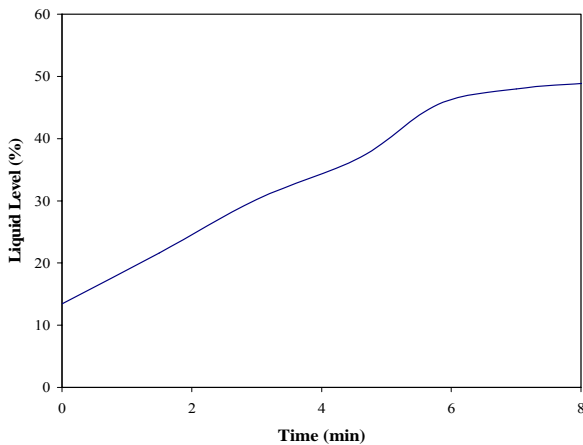

Figure 4: Effect of increasing the flow rate of solvent on liquid level of the main washer

Figure 5 shows the change in mass fraction of 1,3-butadiene in the overhead stream of main washer tower against the same disturbance. This figure illustrates that mass fraction of 1,3-butadiene decreases, because the more flow rate of butadiene will be washed by solvent and go out of the bottom stream.
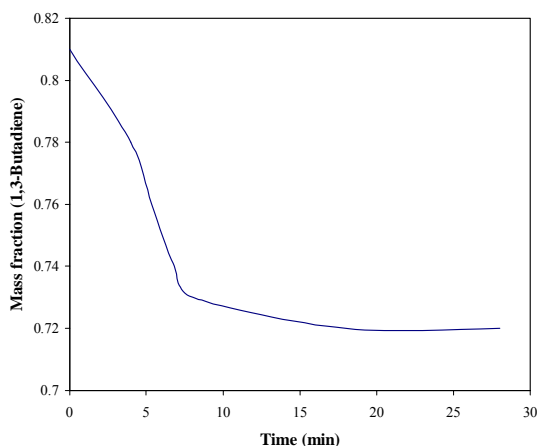

Figure 5: Effect of increasing the flow rate of solvent on mass fraction of 1,3-butdiene in the main washer

Another purpose of dynamic simulation is to study the behavior of the process in some special conditions such as start-up and shut-down. As an example, effect of switching off the after washer bottoms pump on the liquid level of the pump is shown in Figure 6. As shown in this figure, the level of the bottom of the tower which is placed before the pump starts to increase as soon as the pump switches off.. for obtaining a proper response time in comparison with the plant data the volume of the vessel in the bottom of the tower should be exactly as the same as real value.
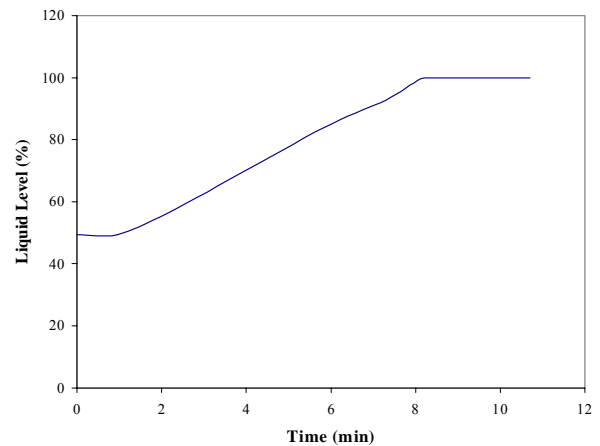

Figure 6: Effect of switching off the pump on the liquid level of the after washer

The stream leaving the after washer bottom is solvent and enters the rectifier. When switching off the pump, the flow of solvent to the rectifier is stopped, thus, the mass fraction of 1,3-butadiene in the side stream that is drawn to after washer and continues to the end of process decreases. Figure 7 shows such a decrease of 1,3-butadiene mass fraction when the flow rate of solvent to the rectifier is stopped.
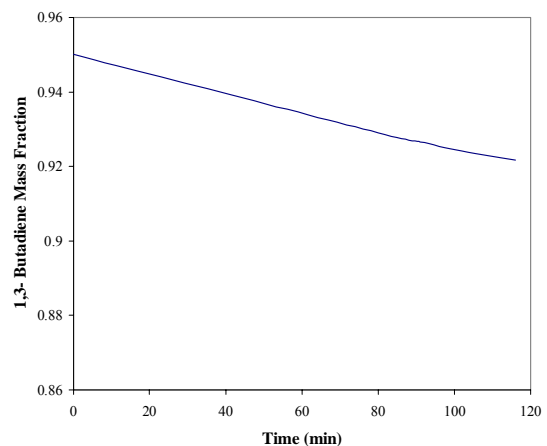

Figure 7: Effect of switching off the pump on the 1,3-butadiene mass fraction in the rectifier side stream

5 CONCLUSIONS

Extractive distillation is more and more commonly applied in chemical industries and becomes an important separation method in chemical engineering. In this work, the BASF butadiene extraction process is simulated in both steady-state and dynamic conditions. Because of using NMP as solvent, which is a non-ideal liquid, NRTL which is an activity model was applied as the thermodynamic model. The binary interaction coefficients were modified according to the components and process conditions in order for the model to best fir the real operating data. The simulation results reported in this paper reveal a good agreement with the operational values in steady state and dynamic modes.

ACKNOWLEDGMENT

NOMENCLATURE

C_s	bias signal of the controller
F_n^L	liquid feed-stream flow rate entering stage n
F_{n-1}^V	vapor feed-stream flow rate entering stage n
h_n^F	molar enthalpy of liquid feed-stream entering stage n
H_{n-1}^F	molar enthalpy of vapor feed-stream entering stage n
K_i	vapor-liquid equilibrium constant
K_c	proportional gain of the controller
L_n	liquid flow rate leaving stage n
L_{n+1}	liquid flow rate entering stage n
M_n	liquid hold up at stage n
S_n^V	vapor side stream flow rate at stage n
S_n^L	liquid side stream flow rate at stage n
t	time
V_n	vapor flow rate leaving stage n
V_{n-1}	vapor flow rate entering stage n
$x_{i,n}$	liquid mole fraction on component i at stage n
$y_{i,n}$	vapor mole fraction on component i at stage n

Greek letters

$\varepsilon(t)$	error function of controller
$C(t)$	output function of controller
τ_D	derivative time constant of controller
τ_I	integral time constant of controller

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